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(21) International Application Number: PCT/EP95/03132 (22) International Filing Date: 7 August 1995 (07.08.95) (30) Priority Data: 9416114.8 10 August 1994 (10.08.94) GB (71) Applicant (for all designated States except AT DE US): SANDOZ LTD. [CH/CH]; Lichtstrasse 35, CH-4002 Basle (CH). (71) Applicant (for DE only): SANDOZ-PATENT-GMBH [DE/DE]; Humboldtstrasse 3, D-79539 Lörrach (DE). (71) Applicant (for AT only): SANDOZ-ERFINDUNGEN VERWALTUNGSGESELLSCHAFT MBH [AT/AT]; Brunner Strasse 59, A-1230 Vienna (AT). (72) Inventor; and (75) Inventor/Applicant (for US only): LEIKAUF, Bernhard [DE/CH]; Dorfstrasse 26, CH-5224 Linn (CH).		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG). Published <i>With international search report.</i>
(54) Title: CEMENT ACCELERATING ADMIXTURE (57) Abstract An accelerating admixture for use with sprayable cementitious compositions such as shotcrete comprises a mixture of (a) amorphous aluminium hydroxide and/or aluminium hydroxysulphate, and (b) at least one amine, preferably an alkanolamine. In a preferred embodiment, the admixture also comprises an aqueous dispersion of at least one polymer which comprises pendant carboxylic moieties.		

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CEMENT ACCELERATING ADMIXTURE

This invention relates to cementitious spraying compositions and to admixtures for use therein.

Cementitious compositions for application to a substrate by spraying, for example, "shotcrete", must be capable of being sprayed in the first place (that is, they must retain sufficient fluidity), and on contacting the surface, they must set quickly (generally within a few minutes) to give a stiff layer to which further layers may quickly be applied. The art-recognised way of achieving this has been the addition at the point of spraying (for example, by injecting into a spray nozzle) of an accelerator in the form of an aqueous solution. The accelerators used are generally strong alkalis such as sodium aluminate, sodium or potassium hydroxide or carbonate and triethanolamine (see, for example, "Concrete Admixtures Handbook", ed. Ramachandran (Noyes, 1984)).

The nature of such substances makes for unpleasant working conditions on spraying sites, and there has long been a need for an effective spraying accelerator which has less of the caustic character of the known accelerators. In a recent development, accelerators comprising amorphous aluminium hydroxide have been proposed. These have the advantage of low alkalinity and high performance. Typical examples of accelerators have been blends of amorphous aluminium hydroxide with gypsum or various water-soluble salts.

Accelerators applied at the nozzle are in liquid form. This means that, in the case of aluminium hydroxide, the solid accelerator must be dispersed in water. This can be done on site, but it is much more convenient if such an accelerator can be supplied in liquid form. This has hitherto not been possible with aluminium hydroxide, dispersions of which are not storage-stable for more than a few days.

It has now been found that a particular combination of aluminium hydroxide with another material not only has excellent storage stability but also is particularly effective as an accelerator for spraying cementitious compositions. There is therefore provided, according to the present invention, an accelerating admixture for use in the spraying of cementitious

compositions, comprising (a) amorphous aluminium hydroxide and/or aluminium hydroxysulphate, and (b) at least one amine.

There is additionally provided a method of preparing a storage-stable, amorphous aluminium hydroxide and/or aluminium hydroxysulphate-based accelerating admixture by
5 the dispersion of amorphous aluminium hydroxide and/or aluminium hydroxysulphate in water, there being additionally added at least one amine.

In the particular circumstances of this invention, aluminium hydroxysulphate is often a better accelerator than aluminium hydroxide and is therefore preferred. It is possible to use a mixture of aluminium hydroxysulphate with aluminium hydroxide and/or aluminium
10 sulphate, but it is preferable to use the hydroxysulphate alone. A typical commercially-available aluminium hydroxysulphate is "Gecedral" (trade mark) L (ex Guilini Chemie GmbH, Ludwigshafen/Rhein, Germany).

The amines for use in this invention should be liquid or soluble in water. A highly preferred class of amines is that of the alkanolamines. The preferred alkanolamines are
15 dialkanolamines and trialkanolamines, more preferably diethanolamine and triethanolamine. Most preferred is a mixture of diethanolamine and triethanolamine.

In an admixture according to the invention, the aluminium hydroxide and/or hydroxysulphate is combined with the alkanolamine in the weight ratio of from 1:10 - 1000:1, preferably from 1:10 - 100:1, more preferably from 1:1 - 10:1. When the preferred
20 mixture of diethanolamine and triethanolamine is used, the ratio of diethanolamine to triethanolamine is from 1:1 to 0:1.

The constituents of the admixture may be added to a spray nozzle separately or preferably as a pre-mixed blend. The invention therefore also provides an accelerating admixture which is a mixture of the aforementioned constituents. In either case the weight ratio of the
25 constituent on cement is from 0.5-10% for the aluminium hydroxide/hydroxysulphate and from 0.001 to 5%, more preferably from 0.001 - 2% or 0.01 - 5% for the amine.

In an especially preferred embodiment of the invention, the accelerating admixture of the invention may be combined with certain other materials to provide particularly outstanding results. The invention therefore also provides a spraying admixture which comprises a combination of an accelerating admixture as hereinabove defined and an aqueous dispersion
5 of at least one polymer which comprises pendant carboxylic moieties.

The polymers useful in this aspect of the invention are any polymers which bear suitable pendant carboxylic moieties. The carboxylic moiety may be a carboxyl group, and any polymer having such groups and complying with the other parameters hereinunder described will work in this invention. Examples include poly(acrylic) and
10 poly(methacrylic) acids and mixtures thereof and copolymers of (meth)acrylic acid with other comonomers. However, preferred polymers are of the "comb" type, that is, polymers comprising a polymer backbone (whose chemical nature is irrelevant to the working of the invention) with carboxyl group-containing moieties pendant therefrom. The moieties may be up to 100 units long and may comprise monomer residues of, for example (meth)acrylic
15 acid, maleic acid or fumaric acid. It is preferred that the moieties be completely made up of (meth)acrylic acid residues.

A preferred backbone is a random addition polymer, one of the monomers of which comprised, prior to polymerization, more than one, and preferably two, polymerizable double bonds. A preferred monomer with more than one double bond is butadiene and a
20 preferred copolymer is a styrene-butadiene copolymer. To such a copolymer (which may have pendant and/or in-chain polymerizable double bonds) carboxyl group-containing monomers such as acrylic acid, methacrylic acid, maleic acid or fumaric acid may be graft copolymerized. Examples of preferred copolymers are styrene-butadiene copolymerized with acrylic acid and styrene/butadiene/maleic (or fumaric) acid terpolymer.

25 The polymers of this invention have molecular weights (weight average) in excess of 20,000 and are solids at room temperature. They also have a limited solubility in water, being at best dispersible (never completely soluble), but they are highly soluble in alkaline media (such as a fluid cementitious mix). In the case of poly(meth)acrylic acid and polymers which are inherently soluble in water, it is possible to prepare such polymers in

such a form that the necessary solubility is achieved, for example, particulate form. They are added to the cementitious mix as an aqueous dispersion of less than 5% solids by weight.

Typical examples of suitable commercial materials are those available under the trade mark
5 "Synthomer" (ex Synthomer Chemie GmbH, Frankfurt/Main, Germany). An especially suitable example is "Synthomer" 9523 (a methacrylic acid-styrene-butadiene copolymer). Another suitable commercial product is "Polyacryl" AD (ex Polygon Chemie AG, Olten, Switzerland)

The aqueous dispersion is added to the cementitious composition at the nozzle, either
10 separately from or in a mixture with the acceleratiing admixture hereinabove described. The proportion of polymer present is from 0.01 to 3% by weight on cement.

When the spraying admixture comprises an aqueous polymer dispersion as hereinabove described, the admixture must be acid, preferably with a pH of 6 maximum. This may be achieved by the addition of an acid, which may be chosen from any suitable strong organic
15 or inorganic acid , which is added in sufficient quantity to achieve the desired pH. In addition, the acid must not react adversely with any of the components of the cementitious composition or the admixture to an unacceptable degree. Reactivity will vary, depending on the individual acid and the components present, but the selection of a suitable acid is not a problem for the skilled person. It is preferred to use a strong mineral acid, and nitric
20 acid has been found to work particularly well in most circumstances.

It has been found that the use of an aqueous polymer dispersion as hereinabove defined in conjunction with an accelerating admixture as hereinabove described enhances the performance of a sprayed cementitious composition considerably. In particular, it appears to enhance adhesion of the sprayed composition to the substrate in the important few
25 minutes after spraying when the hardening of the composition is not sufficiently advanced to ensure good adhesion.

A preferred spraying admixture has the following composition (dry contents, by weight, the

remainder of the formulation to 100% being water):

	aluminium hydroxide/hydroxysulphate	20%	-	60%
	alkanolamine	0.01%	-	25%
	polymer dispersion	0%	-	20%
5	acid	1%	-	20%

A particularly preferred composition has the composition (dry contents, by weight, the remainder of the formulation to 100% being water) .

	aluminium hydroxysulphate	40%	-	60%
	triethanolamine	0.01%	-	20%
10	diethanolamine	0%	-	5%
	acrylic copolymer dispersion	10%	-	20%
	nitric acid	5%	-	20%

The compositions and processes of this invention are useful in the spraying of cementitious composition by both the "wet" and "dry" methods, but they work better in the "wet" method where water is added at the mixing stage prior to pumping. The invention therefore provides a sprayable cementitious composition which comprises an admixture as hereinabove defined.

The sprayable compositions according to this invention may also comprise any of the wide range of other admixtures known to be useful in sprayable cementitious compositions, used in art-recognised quantities. One particularly useful category of admixture is that of the plasticisers and superplasticisers; these can assist in the achievement of a desirable water/cement (W/C) ratio. A further class of useful admixtures are set retarders. Any of the known types may be used, a particularly useful class of materials being phosphonic acid-based materials, in particular those described in United States Patent 4,964,917

A particular feature of the invention is the excellent storage stability of the admixtures

according to the invention. If aluminium hydroxide and/or aluminium hydroxysulphate is dispersed in water, the viscosity rises rapidly to a value which renders the mixture unusable very quickly (typically LVT Brookfield viscosity 100,000+ mPas (Spindle No.4 at 1.5 rpm) a few days after mixing and completely solid after one week). In contrast, an admixture
5 according to the present invention stored at 20°C remains usable for 6 months. Thus, it is possible to prepare admixtures well in advance of use and have them immediately ready, thus reducing the need to mix on site.

Sprayable cementitious compositions which utilize this invention form thick layers which "set up" quickly and can be resprayed without any problems. Rebound characteristics are
10 particularly good, as are both strength development and long term strength. The invention therefore provides the use of a mixture of aluminium hydroxide and/or hydroxysulphate and at least one amine as an accelerating admixture for cementitious compositions which are to be sprayed. The invention further provides a method for the spraying of a cementitious composition on to a substrate from a spray nozzle, wherein there is added to the
15 composition at the nozzle an accelerating admixture as hereinabove defined.

The invention is further described with reference to the following examples in which all parts are expressed by weight.

(a) Preparation of spraying admixture

The following materials are blended under low shear to form a homogeneous mixture:

20	water	55 parts
	aluminium hydroxysulphate ¹	17.9
	triethanolamine	7.7
	diethanolamine	1.55
	65% nitric acid	7.7
25	aqueous polymer dispersion ²	6.15

1. "Gecedral" L ex Guilini Chemie

2. "Synthomer" 9523 ex Trüb Chemie

(b) Testing of spraying admixture

- (i) A spraying concrete mixture is prepared with a W/C ratio of about 0.45. The mixture is sprayed on to a substrate through a nozzle with a dosing at the nozzle with the spraying admixture of 4.8% by weight on cement. It is found that the sprayed concrete goes matt
5 immediately (signifying immediate setting) and that a layer of thickness in excess of 25cm. can quickly be built up with very little rebound. A measurable strength develops after only 6 minutes, and after 16 hours the strength (measured at a number of different points) is between 7 and 18.8 N/mm².
- (ii) The procedure of (i) above is repeated with a dosing of 3.8%. In this case, the
10 thickness readily achievable is about 20cm. and early strength development becomes measurable after about 20 min. After 16 hours, strength is measured and found to be between 14.7 and 19.6 N/mm².

Claims:

1. An accelerating admixture for use in the spraying of cementitious compositions, comprising (a) amorphous aluminium hydroxide and/or aluminium hydroxysulphate, and (b) at least one amine.
- 5 2. An accelerating admixture according to claim 1, wherein the constituents (a) and (b) are components of a single mixture.
3. An accelerating admixture according to either of claim 1 or claim 2, wherein aluminium hydroxysulphate is used and aluminium hydroxide is excluded.
4. An accelerating admixture according to any one of claims 1-3, wherein the amine
10 is an alkanolamine, preferably a dialkanolamine or trialkanolamine, more preferably diethanolamine or triethanolamine, most preferably a mixture of diethanolamine and triethanolamine.
5. An accelerating admixture according to any one of claims 1-4, wherein the
15 admixture additionally comprises an aqueous dispersion of at least one polymer which comprises pendant carboxylic moieties, preferably a "comb"-type polymer.
6. A spraying admixture with the following composition (dry contents, by weight, water to 100%):

aluminium hydroxide/hydroxysulphate	20%	-	60%
alkanolamine	0.01%	-	25%
20 polymer dispersion	0%	-	10%
acid	1%	-	20%
7. The use of a mixture of aluminium hydroxide and/or hydroxysulphate and at least one amine as an accelerating admixture for cementitious compositions which are to

be sprayed.

8. A method of preparing a storage-stable, amorphous aluminium hydroxide and/or aluminium hydroxysulphate-based accelerating admixture by the dispersion of amorphous aluminium hydroxide and/or aluminium hydroxysulphate in water, there
5 being additionally added at least one amine.
9. A method for the spraying of a cementitious composition on to a substrate from a spray nozzle, wherein there is added to the composition at the nozzle an accelerating admixture according to any one of claims 1-6.
10. A sprayable cementitious composition which comprises an admixture according to
10 any one of claims 1-6

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 95/03132

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C04B28/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR,A,2 031 950 (DUFRETHI) 20 November 1970 see claims 1,7	1,2,4
A	---	6-8,10
X	DATABASE WPI Section Ch, Week 7802 Derwent Publications Ltd., London, GB; Class E33, AN 78-03338A & JP,A,52 141 837 (ASADA KAGAKU KOGYO) , 26 November 1977 see abstract	1,4
A	---	6-8,10
A	DE,A,21 22 710 (SIKA AG.) 25 November 1971 see claims 1-5,9	1

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,37 38 258 (INSTITUT FUR STAHLBETON) 29 September 1988 see the whole document ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 015 no. 167 (C-0827) ,26 April 1991 & JP,A,03 037145 (OSAKA CEMENT CO LTD) 18 February 1991, see abstract ---	1
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP 95/03132

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